

Chapter 3.

**γ -ray irradiation induced
mechanical study of WS₂
nanosystems dispersed in
NaCMC polymeric
solution**

3.1 Introduction

Gamma (γ) ray irradiation, a type of ionizing radiation is an efficient strategy to modify the physical and chemical properties of the nanocomposites. It is a simple, user-friendly and high-purity technique to alter the material properties due to its strong penetration power with ultra-uniformity [1,2]. This ionizing radiation leads to atomic displacement, resulting in the electronic excitation of materials, affecting the vital properties of the structure of the materials [3]. When a material is subjected to γ -irradiation, energy deposits in an explicitly localized region, producing ionization, excitation, and the breakage of chemical bonds, along with the formation of numerous free radical species. Thus, the properties of the materials can be altered through these free radicals by reacting with the nearby elements [4]. Studies have also been carried out to modify the fabricated nanocomposites, filler materials, or raw polymers by employing charge particle irradiation, electron beam, focused ion beam, or UV rays [5]. Recent articles have shown that extensive use of γ -rays can modify the physicochemical properties of 2D nanosystems, thereby promoting chemical reactions to occur on the surfaces [6]. It is an effective technique for altering material morphology and surface structure through the creation of defects, vacancies, dislocations, etc. [7]. There are limited reports on the studies of the effect of γ -ray irradiation on the properties of 2D TMDC systems. In an article, Felix *et al.* reported ferromagnetic hysteresis due to the presence of defect configuration on single-layer WS₂ crystals exposed to 400 Gy γ -dose using ⁶⁰Co as the source of radiation [8]. Isherwood *et al.* studied the effect of γ -dose after an adsorbed dose of 500 kGy on the MoS₂ system and observed edge-selective etching due to the reduced rate of reaction between the MoS₂ layer and radiolytic adsorbates [9]. In a very recent article by Jadhav *et al.*, γ -irradiation at a dose of 50 kGy and 500 kGy showed a 10- to 100-fold increase in saturation current, exhibiting profound enhancement in the electrical properties of WS₂ material [10].

The addition of TMDC materials like WS₂ into the polymeric matrix can also improve mechanical and electrochemical sensing properties [11,12]. However, the mechanical strength of 2D layered WS₂ nanosystems dispersed in a polymer namely, sodium salt of carboxymethyl cellulose (NaCMC) under radiation exposure has not yet been explored. It was known that NaCMC is a polysaccharide, which is a water-soluble cellulose derivative containing carboxymethyl groups (-CH₂-COOH) attached to some of the hydroxyl groups of glucopyranose monomers [13,14]. Cellulose and its derivatives

have been increasingly used in various fields, such as corrosion inhibition, due to their eco-friendly, biodegradable nature, etc. As an anionic polyelectrolyte, CMC has also been widely utilized for its colorless and optical transparency, film-forming ability, elasticity and tensile strength, flexibility and resilience, low toxicity and non-allergenic properties, as well as superb hydrophilicity [15,16].

This chapter examines the effects of γ -irradiation on exfoliated WS₂ systems, with doses ranging from 10 kGy to 40 kGy. The irradiation doses in this study were selected within a moderate range of gamma (γ) ray exposure, based on insights gained from previously reported works. For instance, Wu *et al.* utilized a γ -ray dose of 30 kGy to investigate the frictional and electrical properties of the analogous WSe₂ system [17]. In a previous study by our group, a phase transition from hexagonal to trigonal WS₂ was witnessed at a high enough γ -dose of 96 kGy [18]. Furthermore, Li *et al.* noted that mild to moderate γ -irradiation can have beneficial effects on layered graphitic materials [19]. This is particularly relevant, as a higher number of γ -photons would produce a greater density of recoiled electrons, which in turn could lead to increased structural disorder or localized amorphization within the material.

The structural, vibrational, and elemental compositional study of WS₂ after irradiation were analyzed using XRD, Raman, and XPS analysis to understand the effect of γ -photon exposure. Later, the γ -irradiated WS₂ nanosystems were dispersed in a host matrix NaCMC polymeric solutions to make films for mechanical studies. The tensile properties of free-standing WS₂/NaCMC nanocomposite films were investigated before and after irradiation at critical doses of lower (10 kGy) and higher (35 kGy) doses of γ -ray exposure for varied wt.% concentrations.

The exfoliated WS₂ systems were kept in a γ -irradiation chamber available at UGC-DAE CSR, Kolkata, for the irradiation experiment. Here, ⁶⁰Co was chosen as a source of γ -irradiation, imparting energy of ~1.3 MeV at a dose rate of 1.75 kGy/h under an ambient temperature of ~300 K. The samples were marked for 0 kGy (un-irradiated), 10 kGy, 25 kGy, 30 kGy, 35 kGy, and 40 kGy. The samples were extracted from the chamber after being exposed for the specified duration, offering suitable doses of interest.

3.2 Physical properties of γ -irradiated WS₂/NaCMC films

3.2.1 Structural and vibrational features of γ -irradiated WS₂ nanosystems

The powder X-ray diffraction (XRD) patterns of the un-irradiated and exfoliated sheets of WS₂ exposed to γ -rays with doses between 10-40 kGy can be found in Fig. 3.1(a). The diffraction peaks shown are obtained in the range of Bragg's diffraction angle, $2\theta = 10^\circ$ - 70° . The peaks situated at $2\theta \sim 14.6^\circ$, 29.05° , 44.25° , and 60.11° corresponded to (002), (004), (006), and (008), respectively and are indexed to the hexagonal crystal structure of WS₂ featuring space group *P63/mmc* in the JCPDS card no. 08-237 [20,21]. The (002) peak appeared to be the preferred orientation of the crystallites, signifying a high degree of crystallinity along the *c*-axis direction (Fig. 3.1(b)). In addition, the lattice parameters, average crystallite sizes, and micro-strains caused by stress resulting from lattice distortions after radiation exposure were estimated by analyzing the XRD patterns, as

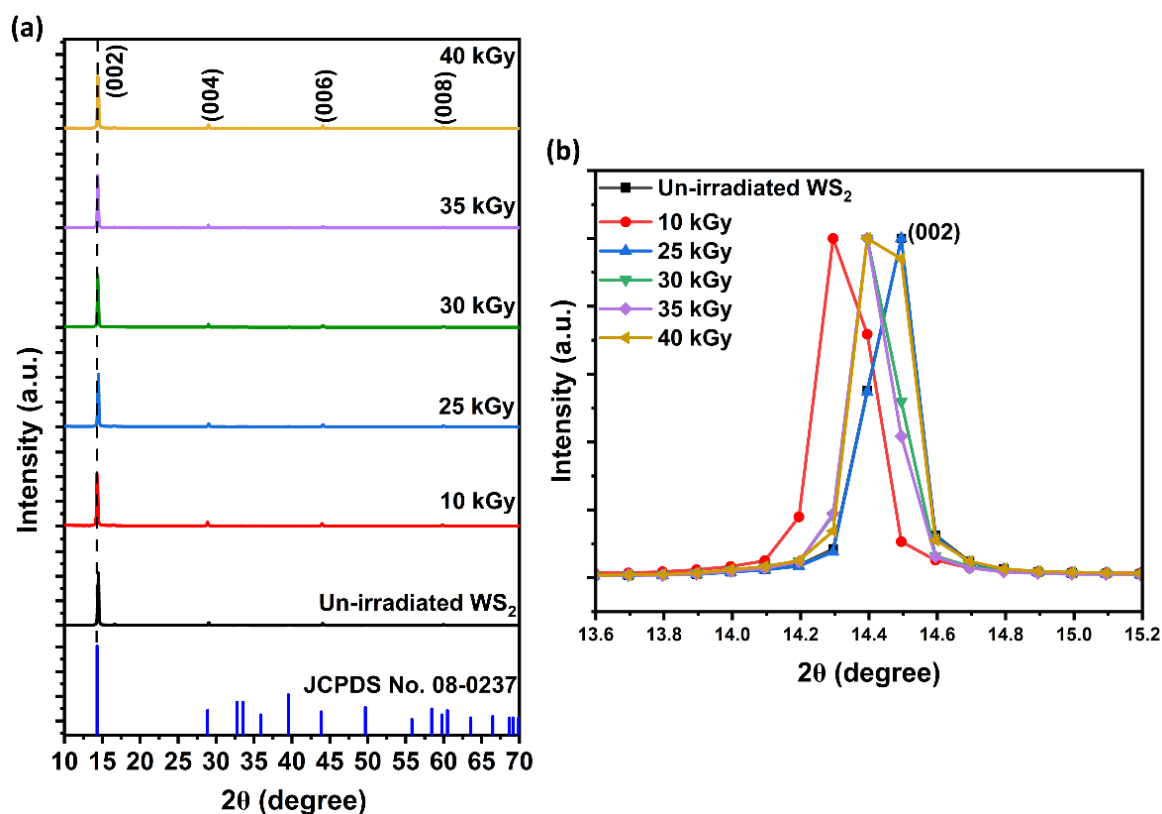


Figure 3.1: (a) Powder XRD patterns of un-irradiated and irradiated WS₂ exposed to 10-40 kGy doses of γ -rays, (b) plots showing the (002) peak oriented along the *c*-axis direction of the hexagonal phase structure of WS₂ system.

Table 3.1. Structural parameters of WS₂ systems upon γ -irradiation at 10-40 kGy.

Sl. No.	Sample (WS ₂)	Lattice parameter along <i>c</i> -axis (Å)	Average crystallite size, <i>d_c</i> (nm)	Micro-strain, $\epsilon \times 10^{-3}$
1	Un-irradiated	12.24	69.9	0.41
2	10 kGy	12.35	46.8	0.74
3	25 kGy	12.24	64.2	0.54
4	30 kGy	12.28	48.2	0.72
5	35 kGy	12.28	49.5	0.70
6	40 kGy	12.26	55.9	0.62

shown in Table 3.1. The crystallite sizes, exhibiting anomalous variations, were observed to decrease when exposed to high-energy γ -photons, reducing from ~ 70 nm to as small as ~ 47 nm within the dose range of 10-40 kGy. Slightest alteration in lattice constant, but an observable change in average crystallite sizes can be found with an increase in γ -dose. Due to high-energy γ -irradiation, which ionizes the atomic or molecular sub-lattices of the system under study, ample point defects or vacancies are likely to form. It is worth mentioning here that, atomic masses of the corresponding constituents and radiation dose would play a decisive role in modifying the structure of the WS₂ system [22]. The accumulation of irradiation-induced defects leads to lattice distortions and a slight expansion of the crystal structure, shifting the XRD peaks toward lower Bragg angles with increasing γ -dose. The non-uniform distribution of these distortions contributes to peak broadening, signifying the development of micro-strain within the irradiated material. At higher doses, these deformations or defects increase the internal stress locally, influencing the lattice structure and diminishing the crystallites into smaller ones. However, the effect follows an anomalous trend. These anomalous variations indicate competing events occurring due to γ -irradiation, leading to the accumulation of defects on the surface of WS₂ layers, fragmentation, and recrystallization of grains at comparatively higher doses.

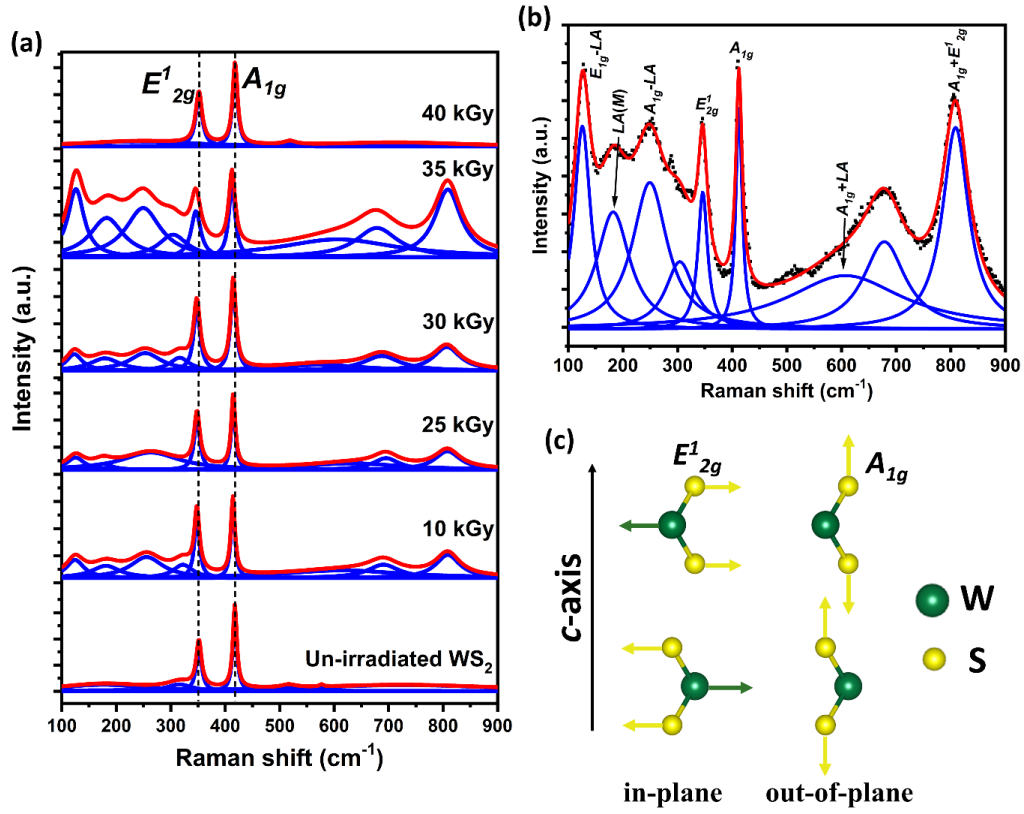


Figure 3.2: (a) Raman spectra of un-irradiated WS₂ and WS₂ irradiated with γ -ray exposure varied at doses from 10-40 kGy along with multi-peak Lorentzian fit, (b) deconvoluted Raman spectra at 35 kGy with second-order Raman modes due to irradiation effect, (c) schematic representation of the direction of the in-plane (E'_{2g}) and out-of-plane (A_{1g}) vibrational modes.

The Raman spectra of the un-irradiated WS₂ and irradiated with γ -rays at varied doses of γ -rays of 10 kGy, 25 kGy, 30 kGy, 35 kGy and 40 kGy, respectively, plotted with multi-peak Lorentzian fittings are shown in Fig. 3.2. The intense in-plane (E'_{2g}) and out-of-plane (A_{1g}) first-order Raman modes emerge at 352 cm⁻¹ and 418 cm⁻¹, respectively (Fig. 3.2(a)). Additionally, the well-resolved Raman spectra in the case of 35 kGy reveal the evolution of second-order Raman signatures due to radiation exposure. These peaks were attributed to the $E'_{2g} - LA$, $A_{1g} - LA$, $A_{1g} + LA$, $4LA$ and $A_{1g} + E'_{2g}$ modes appearing at ~128 cm⁻¹, 248 cm⁻¹, 606 cm⁻¹, 678 cm⁻¹, and 808 cm⁻¹, respectively (Fig. 3.2 (b)) [21,23]. The peak revealed at ~178 cm⁻¹ is attributed to the $LA(M)$ mode, indicating the presence of defects in the WS₂ system that have become more prominent after irradiation at a dose range of 10-35 kGy [24,25]. Moreover, the intensity ratios were calculated considering the E'_{2g} and A_{1g} modes in the Raman spectra for varied doses of γ -irradiation. The highest ratio, ~0.79, observed at the first dose shown in Table 3.2, indicates radiation-assisted exfoliation in the layered WS₂ system. At higher doses, the γ -irradiation predominantly

Table 3.2. Raman modes identification and intensity ratios were investigated from the acquired Raman spectra.

Sl. No.	Sample (exfoliated WS ₂)	Peak position (cm ⁻¹)		E'_{2g}/A_{1g} (Intensity ratio)
		E'_{2g} mode	A_{1g} mode	
1	0 kGy	352	418	0.55
2	10 kGy	348	414	0.79
3	25 kGy	349	414	0.72
4	30 kGy	347	414	0.70
5	35 kGy	347	412	0.50
6	40 kGy	352	418	0.63

induces chalcogen vacancies, leading to a decrease in the intensity up to 35 kGy, possibly due to the disruption of bonds between the tungsten (W) and sulfur (S) atoms. Again, at the maximum dose of 40 kGy, a structural rearrangement of atoms would occur, causing the E'_{2g} -to- A_{1g} intensity ratio to augment again.

3.2.2 Elemental compositional analysis

The elemental compositions and chemical state of un-irradiated and γ -irradiated WS₂ systems were investigated using an XPS study, shown in Fig. 3.3. The XPS survey scans of un-irradiated WS₂ and after γ -irradiation at 10 kGy and 35 kGy can be found in Fig. 3.3(a). The presence of W 4*f* and S 2*p* core-level spectra was confirmed in the survey spectra of WS₂ systems. In addition, binding energy peaks corresponding to C 1*s*, N 1*s*, and O 1*s* could be observed due to environmental contaminants or during sample processing. From the W 4*f* core level spectra, the resolved plots of W 4*f* core level spectra display doublet species, W 4*f*_{7/2} and W 4*f*_{5/2} states of tungsten species, resulting in peaks at ~32.4 eV and ~34.6 eV, respectively. A broad peak at around ~37.8 eV represents the W 5*p*_{3/2} state of tungsten shown in Fig. 3.3(b) [26]. We can observe minute shifting in the W 4*f*_{7/2} states by ~0.1 eV and ~0.3 eV towards lower binding energy at low and higher doses of γ -ray irradiation, respectively, along with a shift in the W 4*f*_{5/2} states by ~0.1 eV and ~0.2 eV. Thus, these peaks belong to the W⁴⁺ oxidation state of the 2*H*-WS₂ phase. Additionally, a small shoulder peak appears at around 35.8 eV, corresponding to the W-O bond and indicative of the W⁶⁺ oxidation state [27]. This peak associated with W-O reduces

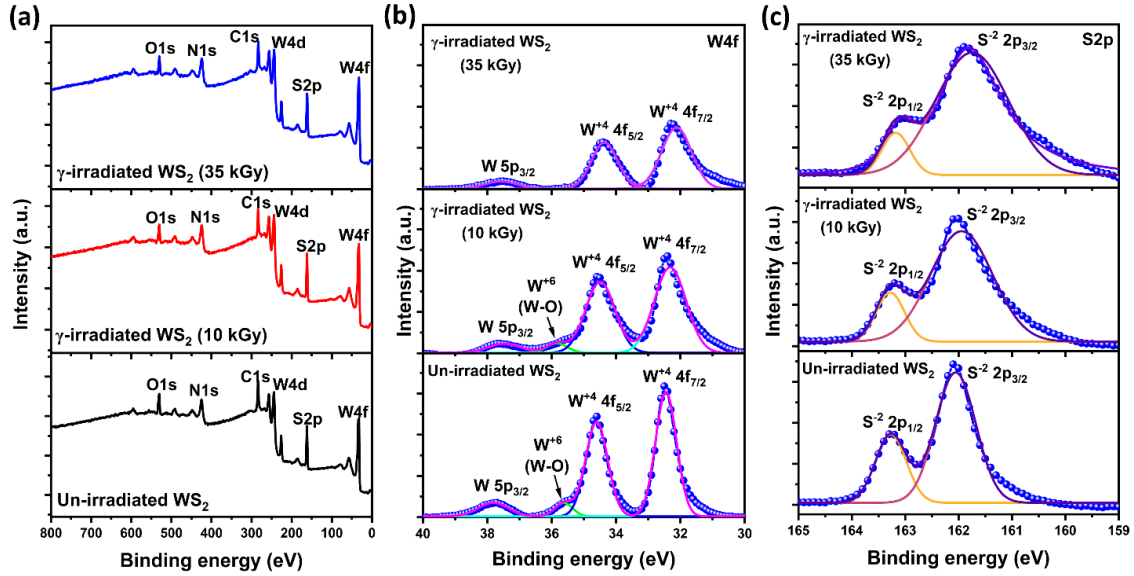


Figure 3.3: (a) XPS survey scan, (b) W 4f-core level spectra, (c) S 2p-core level of un-irradiated and γ -irradiated WS₂ at 10 kGy and 35 kGy, respectively.

with γ -irradiation and completely disappears at a high γ -dose of 35 kGy, owing to changes in the chemical environment of the WS₂ systems. Furthermore, the resolved plots of S 2p core-level spectra reveal peaks at ~ 162.1 eV and ~ 163.3 eV ascribed to S 2p_{3/2} and S 2p_{1/2} states of divalent sulfide ions (S²⁻) of un-irradiated WS₂ (Fig. 3.3(c)) [28,29]. Similarly, peaks were observed in γ -irradiated WS₂ systems at different doses of 10 kGy and 35 kGy, with a slight shift toward lower binding energies in the S 2p_{3/2} states by ~ 0.1 eV and ~ 0.3 eV, respectively. This shift in the W 4f and S 2p core level spectra indicates a sulfur deficiency, and thus, reduced to WS_{2-x} phase as a result of γ -irradiation [30]. Moreover, a decrease in the peak intensity as well as broadening in the core-level spectra of W 4f and S 2p with radiation exposure further advocates variations in the atomic compositions in the WS₂ system due to γ -impact [31]. The dislodgment of atoms in the structurally ordered lattice, with sulfur vacancies being the most probable event that would lead to the suppressed peak intensity in the core-level spectra.

3.3 Mechanical properties of γ -irradiated exfoliated WS₂ dispersed in NaCMC

3.3.1 Load bearing capacity, elasticity, and breaking points

The tensile properties of γ -irradiated WS₂ nanosystems were studied by dispersing them in the NaCMC polymeric host matrix. Both wt.% and γ -dose aspects have been considered independently while acquiring data. To attain superior mechanical properties for the WS₂ nanosheets, adequate interfacial interaction between the nanosheets and the host matrix is

essential. Consequently, the homogenous dispersion of the nanosheets in the matrix plays a vital role. The polymeric composites containing γ -irradiated WS₂ systems were developed to form nanocomposite films and subsequently studied using stress-strain curves, shown in Fig. 3.4(a-c). The stress-strain curves acquired can essentially be divided into two distinct segments: (a) the elastic, and (b) the plastic regions. The elastic region spans a strain range of approximately 40-80% based on the sample specimen, un-irradiated, or irradiated with γ -dose, and with the extent of loading. Beyond this linear region, plastic deformation occurs and is characterized by strain hardening. This plastic regime follows a growing trend independently. Herein, a comparable elongation percentage occurs for a higher amount of tensile stress, and upon achieving maximum strain, the breaking point is attained.

Moreover, corresponding to different strain values, there is a slight change in the stress level of the irradiated WS₂ systems subjected to γ -ray exposure of 10 kGy and 35 kGy and at a loading of 0.5 wt.% as compared to their un-irradiated counterpart. Specifically, the elongation at break was seen declining with increasing irradiation dose. Further, at 1 wt.% and 5 wt.% of WS₂ loading, there is an anomalous increase in the magnitude of the stress in the irradiated cases of 10 kGy and 35 kGy. This signifies that ultimate tensile strength increases with higher breaking stress for irradiated systems with an augment of WS₂ loading in the NaCMC host matrix at 1 wt.% and 5 wt.% offering respective augments of 83%, and 45% eventually. A substantial enhancement in the ultimate tensile strength could be observed from the stress-strain curve in the case of 1 wt.% WS₂/NaCMC nanocomposite system compared to the pure NaCMC (included in *Appendix* (Fig. A1)) and at a lower γ -dose of 10 kGy. The better reinforcement ability of WS₂ as a filler material in the NaCMC polymeric host matrix at 1 wt.%, together with better interfacial interaction, is expected to enhance the tensile property at large [32,33]. This also implies an effective transfer and load-bearing capacities of the nanocomposites due to an adequate filler distribution within the polymeric matrix. In addition, the large surface area of the WS₂ nanosheets used as nanofillers plays a crucial role in determining the mechanical properties of the nanocomposite systems. However, at higher loading concentrations, agglomeration and re-stacking of sheets due to van der Waal interaction between the layers would lower the surface area, and the interfacial interaction between the guest WS₂ and the host matrix of NaCMC [34,35]. As a result, the tensile strength at

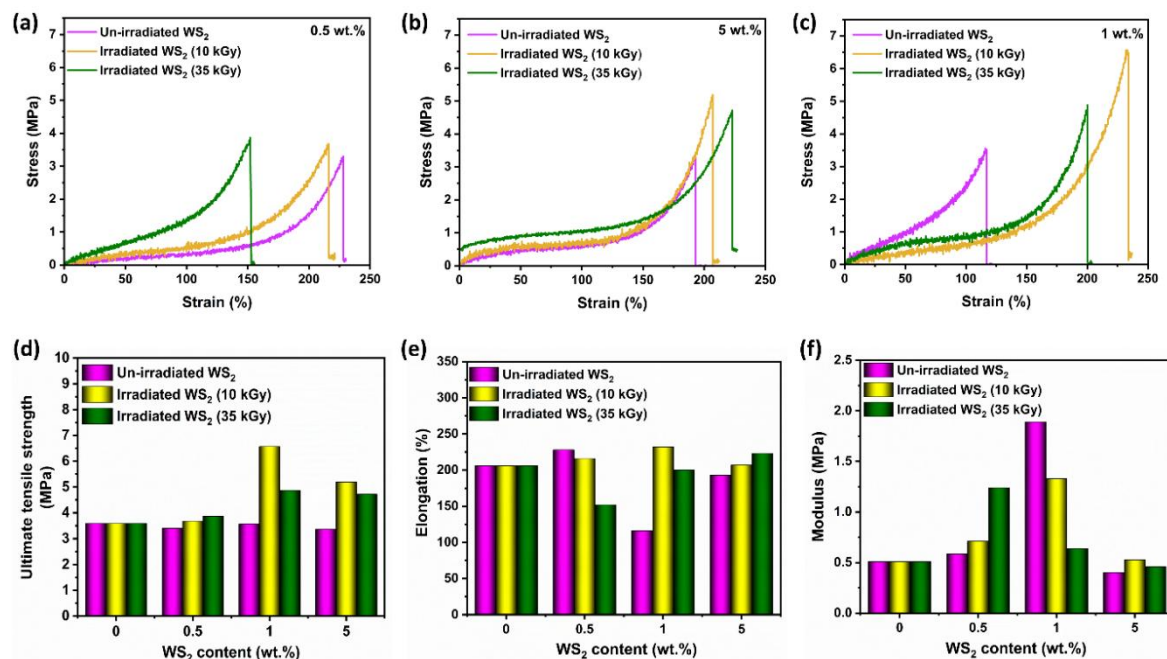


Figure 3.4: Mechanical stress vs. strain plot at a strain rate of 5 mm/min of WS₂/NaCMC nanocomposite films plotted for (a) 0.5 wt.%, (b) 1 wt.% and (d) 5 wt.% of un-irradiated WS₂, and γ -irradiated WS₂ at 10 kGy, 35 kGy, respectively. A comparative view of un-irradiated and irradiated WS₂ at 10 kGy and 35 kGy to variation in (d) ultimate tensile strength (MPa), (e) elongation at break (%), and (f) Young's modulus (MPa) with varied concentrations of WS₂ content in wt.% are shown.

higher γ -doses of WS₂ nanosheets gets lowered. A comparison of un-irradiated and irradiated WS₂ at doses of 10 kGy and 35 kGy is presented, highlighting the changes in ultimate tensile strength (MPa), elongation at break (%), and modulus (MPa) across various WS₂ content in wt.% (Fig. 3.4(d-f) & Table 3.3). The elongation at break was maximum (up to ~228%) in the un-irradiated case and for the lower loading level (0.5 wt.%) of WS₂ content. With higher loadings of WS₂, such as 1 wt. % and 5 wt.%, the elongation at break shows up for irradiated cases at 10 kGy and 35 kGy of γ -ray exposure. This signifies that the specimen tends to become ductile after being exposed to γ -dose, and was more prominent at higher loadings of WS₂ content. Consequently, the mechanical properties exhibited an enhanced tensile strength, ductility, and flexibility for 1 wt.% of WS₂/NaCMC nanocomposite film, considering WS₂ at a γ -dose of 10 kGy. It is imperative to note that, due to uneven solvent drying, slight variations in film thickness might occur during the solvent evaporation process.

Table 3.3. Parameters related to the mechanical properties of WS₂/NaCMC composites using un-irradiated (0 kGy) and γ -irradiated (at 10 kGy and 35 kGy) WS₂ fillers at varied loading wt.% in the polymer.

Sl. No.	Samples	Ultimate tensile stress (MPa)			Elongation (%)			Youngs modulus (MPa)		
		0 kGy	10 kGy	35 kGy	0 kGy	10 kGy	35 kGy	0 kGy	10 kGy	35 kGy
1	0.5 wt.% WS ₂ /NaC MC	3.4	3.68	3.87	228	216	152	0.584	0.711	1.24
2	1 wt.% WS ₂ /NaC MC	3.56	6.57	4.87	116	232	200	1.89	1.33	0.638
3	5 wt.% WS ₂ /NaC MC	3.36	5.19	4.72	193	207	223	0.401	0.526	0.458

An unusual trend in stress-strain response was observed in the case of un-irradiated WS₂ at 1 wt.%, leading to a higher modulus value of 1.89 MPa, making the composite stiffer. However, the stiffness remained insensitive to the strain rates after γ -ray exposure. The γ -irradiation creates vacancies or point defects and promotes atomic reorganization locally. Here, we speculate structural reordering with defect manifestation that would account for interconnected structures within the cellulose host matrix. Nevertheless, when the dose range increases significantly, an increase in internal stress can cause lattice distortion, resulting in agglomeration of sheets, thereby disrupting the interfacial growth of WS₂ nanofiller and host matrix [19].

Additionally, the Young's modulus (initial elastic slope), which reflects the material's initial elastic stiffness, exhibits minimal variation across the applied strain range with irradiation. To be mentioned, γ -irradiation is known to induce structural changes in the WS₂ system, such as bond weakening and lattice distortion, which can contribute to a reduction in modulus under certain conditions. Nonetheless, factors like the presence of microcracks, voids, and the uneven clustering of WS₂ nanofillers may contribute to a reduction in modulus. The reason behind these features could be understood through the morphological analysis of the fractured surfaces of the WS₂/NaCMC nanocomposite films discussed in the next section.

3.3.2 Reinforcement mechanisms of the fractured surfaces

The morphological analysis of the fractured surfaces and their reinforcement mechanisms developed in the WS₂/NaCMC composite films are shown through the FE-SEM images. The morphological features of pure NaCMC and exfoliated thinner nanosheets before being exposed to γ -irradiation can be found in Fig. 3.5. The exfoliated sheets possess a layered morphology that has a large surface area and lateral diameters of ~ 1 -2 μm . The fractured structures of the composite systems show ample rough surfaces, indicating ductile failure in the tensile test [36]. The morphological features of un-irradiated WS₂ before and after tensile load are shown in Fig. 3.6. The microstructure of 1 wt.% WS₂/NaCMC nanocomposite films before and after the tensile test show some interconnected patterns due to the percolation of polymeric cellulose into the associated gaps of WS₂ nanosheets (Fig. 3.7 A(a,b)). These films displayed tightly packed structures with no visible voids, microcracks, or signs of interfacial debonding on the surface, indicating adequate adhesion between the matrix and the filler. The surface morphology

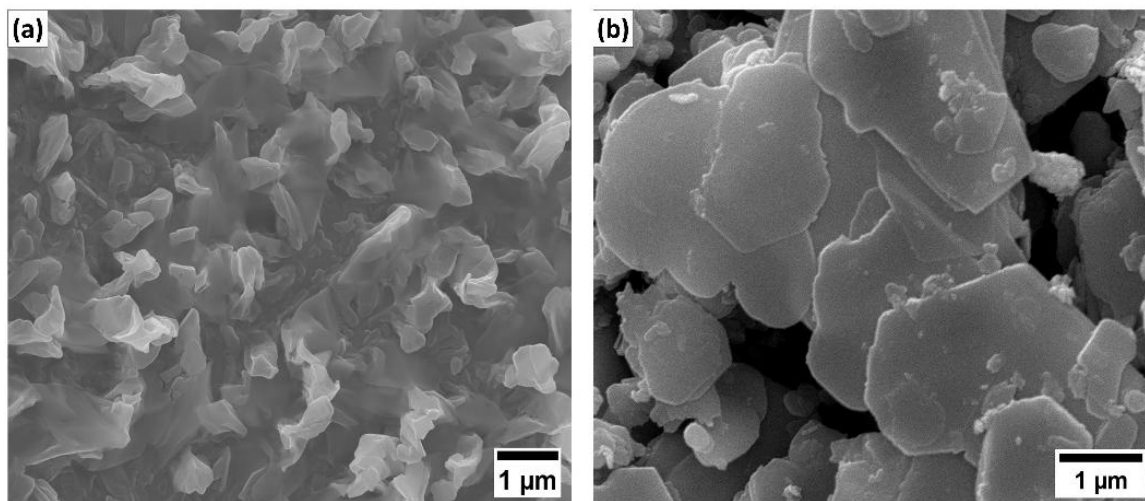


Figure 3.5: FE-SEM images of (a) pure NaCMC film and (b) exfoliated WS₂ nanosheets without NaCMC.

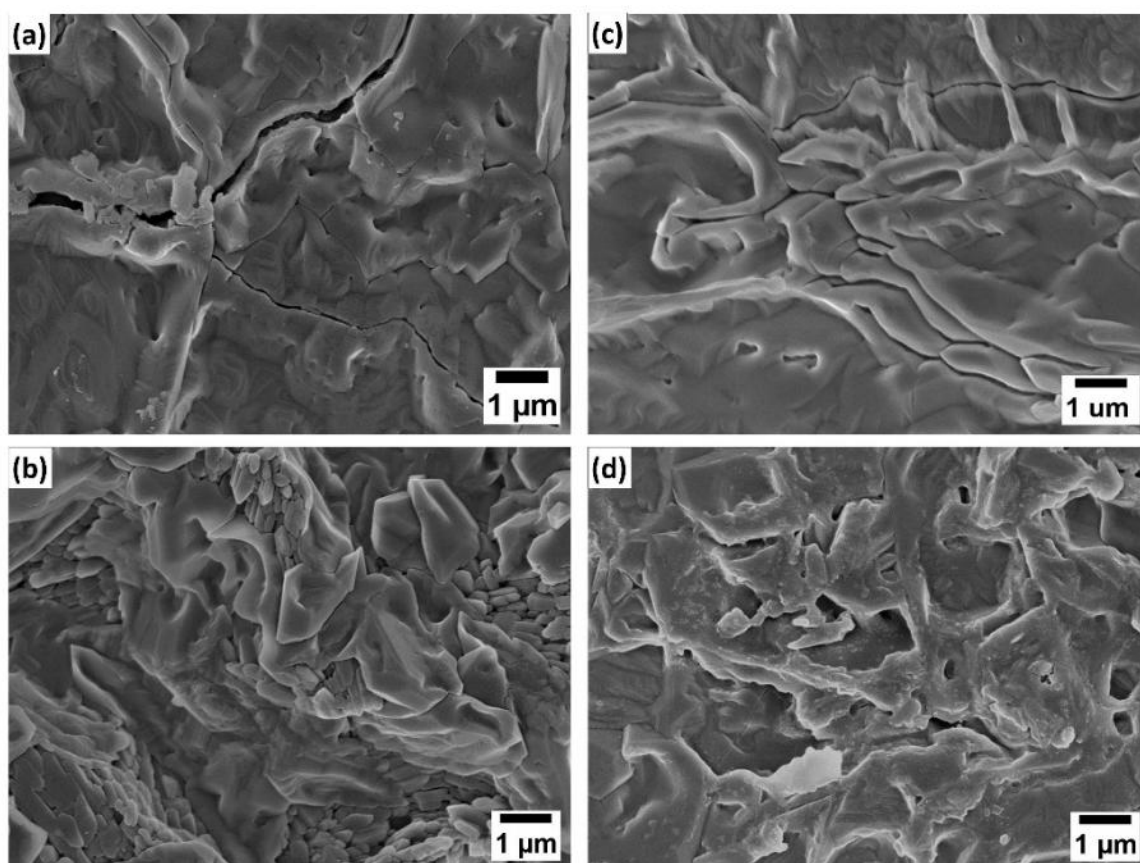


Figure 3.6: FE-SEM images of un-irradiated WS₂/NaCMC (upper panel) before stress is applied and (lower panel) with strain, i.e. after stress is released, respectively for (a,b), 1 wt.%, (c,d) 5 wt.% loading of WS₂.

also lacked large agglomerates, further suggesting adequate dispersion and interfacial compatibility. These microstructures between the polymer and WS₂ nanofillers contributed to the enhanced tensile strength observed at a γ -dose of 10 kGy. These structured networks also played a role in enduring crack propagation in the material, thus improving mechanical strength. Notably, the WS₂/NaCMC nanocomposite films irradiated at 10 kGy, particularly with 1 wt.% loading, exhibited a significant augment in energy absorption capacity and the area under the stress-strain curves at higher strain rates, featuring a more ductile response [37].

At a higher γ -dose of 35 kGy, the tensile strength decreased compared to that at 10 kGy. This reduction was attributed to radiation-induced micro-damage, where lattice distortions led to increased internal stress, creating voids within the material structure [38]. These structural changes led to the clumping of WS₂ at 1 wt.%, adversely affecting the mechanical performance. At 5 wt.%, microcracks have evolved in the WS₂/NaCMC

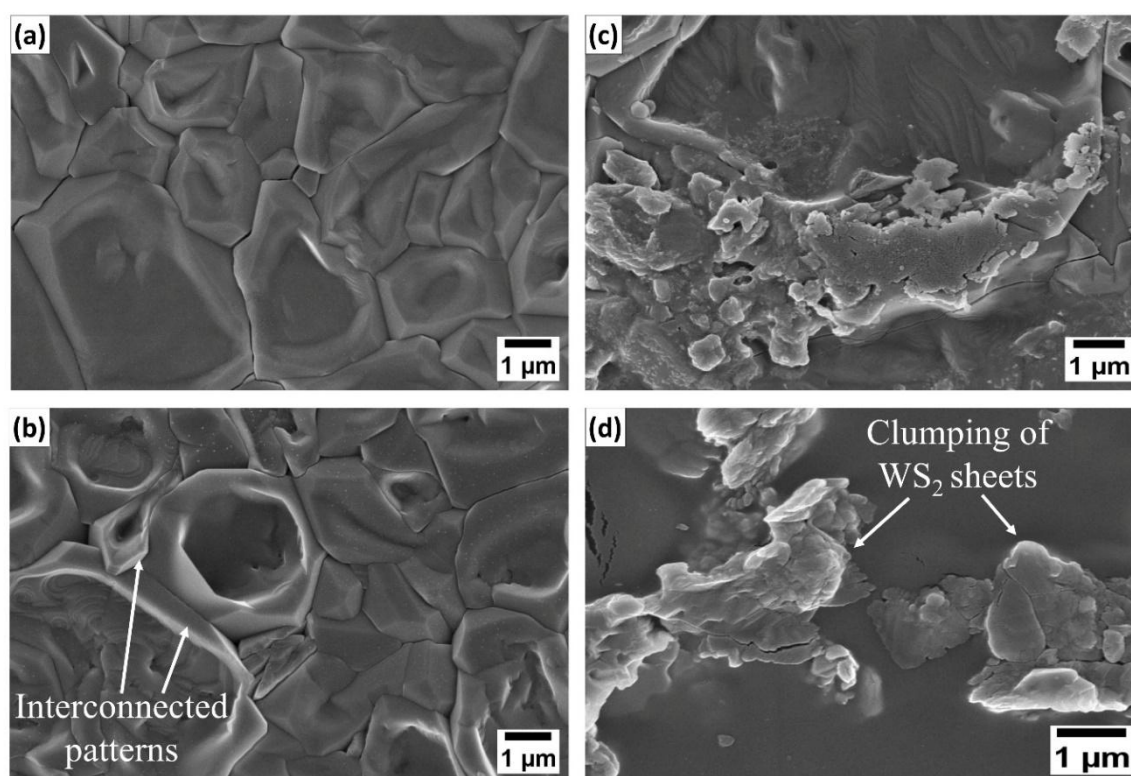


Figure 3.7 (A). FE-SEM images of the reinforcement mechanisms developed in 1 wt.% WS₂/NaCMC nanocomposite films, before (upper panel) and after (lower panel) applying strain, respectively, upon exposure to γ -rays at (a,b) 10 kGy, and (c,d) 35 kGy.

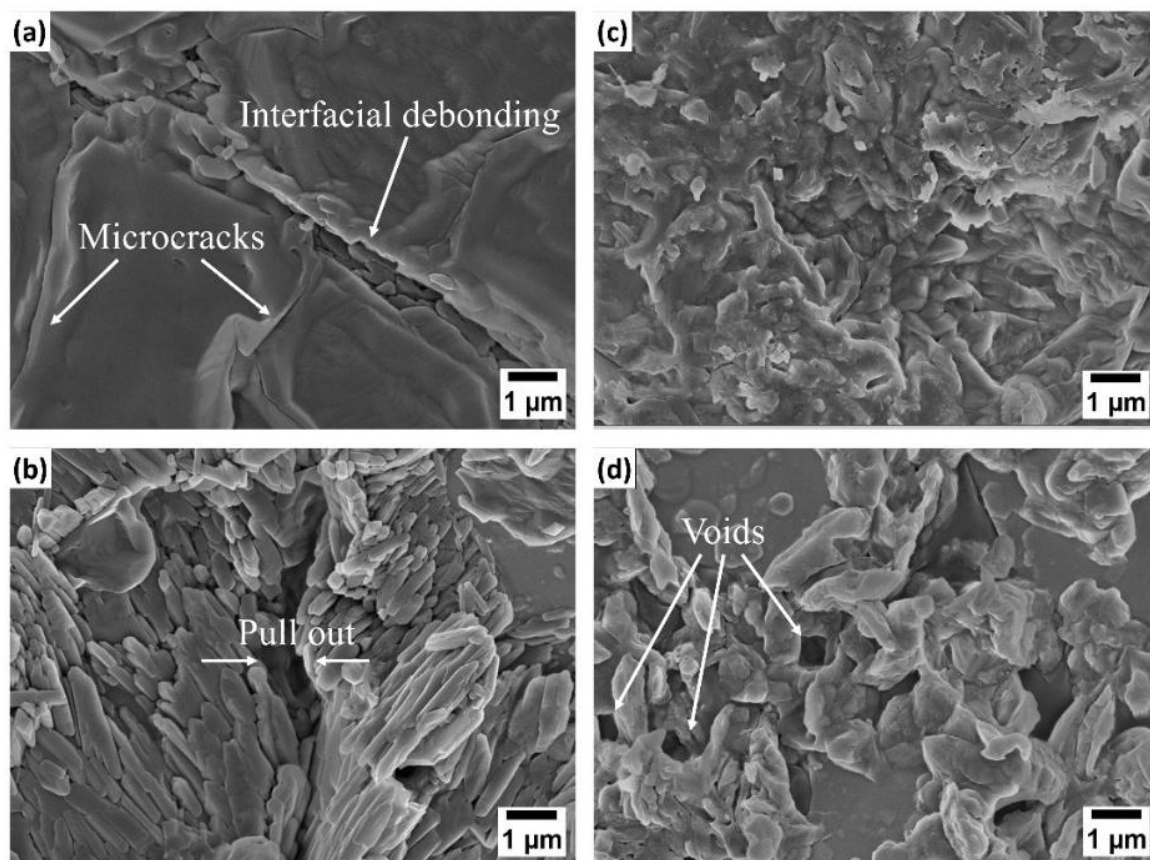


Figure 3.7 (B): FE-SEM images of the reinforcement mechanisms developed in 5 wt.% WS₂/NaCMC nanocomposite films, before (upper panel) and after (lower panel) applying strain, respectively, upon exposure to γ -rays at (a,b) 10 kGy, and (c,d) 35 kGy.

composite films of 10 kGy γ -dose. This was primarily driven by micro-damage mechanisms such as crack propagation and interfacial debonding. These were likely to be due to stress concentrations caused by interfacial voids and cracks around micron-sized filler material that appeared in the form of elongated structures within the polymeric NaCMC matrix, observed in Fig. 3.7 B(a,b). Such microcracks led to the collapse of the interconnected microstructures, ultimately resulting in reduced mechanical strength [39]. This is an intrinsic toughening mechanism developed to improve the fracture resistance of low-toughness materials. In addition, it signifies poor interfacial bonding at the interface [40]. Thus, crack propagation, interfacial debonding and pull-out of fractured WS₂ nanosheets mostly contribute to the fracture toughness of the nanocomposites. Moreover, the surface structures of higher doses of γ -rays display complex textures with irregular patterns across their entire surface, resulting in voids and cracks in their microstructure due to clustering of WS₂ sheets in the case of 1 wt.% and 5 wt.% cases (Fig. 3.7 A (c,d) and

Fig. 3.7 B (c,d)). As a result, the tensile strength at a 35 kGy dose was comparatively lower than that at a 10 kGy dose. Thus, the mechanical properties of WS₂/NaCMC nanocomposite films are significantly influenced by the type of irradiation dose considered, and consequently, by the morphological evolution, defect formation, and stress accumulation in the system under study [41].

3.4 Concluding remarks

In conclusion, this chapter explores the mechanical properties of WS₂/NaCMC nanocomposite systems following γ -ray exposure to exfoliated WS₂ systems. Before analysing these properties, a structural study was conducted on the WS₂ system both before and after irradiation, without incorporating it into the NaCMC matrix. Here, the XRD analysis confirms that WS₂ has a hexagonal phase structure (*P63/mmc* space group) and is oriented along the *c*-axis. Raman spectroscopy reveals mixed modes in γ -irradiated WS₂, with first-order Raman modes appearing at 352 cm⁻¹ (*E'*_{2g} mode) and 418 cm⁻¹ (*A*_{1g} mode). Additionally, prominent defect-mediated *LA* modes emerge near 178 cm⁻¹, particularly at a γ -dose of 35 kGy. The XPS analysis of the W 4*f* and S 2*p* core-level spectra indicates that exfoliated WS₂ retains its 2*H* phase with W⁴⁺ and S²⁻ oxidation states. Moreover, γ -ray exposure leads to peak broadening and reduced intensity in the core-level spectra of W 4*f* and S 2*p* compared to un-irradiated WS₂, suggesting structural modifications.

As for the mechanical study, stress-strain analysis was conducted, revealing an elastic strain range of around 40-80%, depending on the nature of WS₂ loading and γ -ray dose. Beyond this range, plastic deformation occurs, exhibiting strain-hardening before failure. The ultimate tensile strength increases with higher WS₂ nanofiller loadings, as can be observed in irradiated systems. Specifically, WS₂/NaCMC nanocomposites offer an increase in tensile strength up to 83% and 45% at 1 wt.% and 5 wt.%, respectively. Notably, mechanical properties, including tensile strength, ductility, and flexibility, are significantly enhanced at 1 wt.% of the composites, particularly at a γ -dose of 10 kGy. Thus, irradiation alters the lattice structure of materials, enhancing the transfer efficiency and interfacial bonding between WS₂ nanofillers and the NaCMC polymer matrix at low doses.

However, microstructural analysis reveals the formation of microcracks and stress concentration zones in the WS₂/NaCMC composites, particularly at higher nanofiller loadings and radiation doses. These suggest that while low-dose γ -radiation can enhance

tensile properties, excessive exposure may lead to increased internal stress, lattice distortions, and structural defects. This, in turn, promotes agglomeration and void formation, ultimately diminishing the mechanical performance of the composites.

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